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TECHNICAL MEMORANDUM

No. 1084

KINETICS OF CHEMICAL REACTIONS IN FLAMES

By Y. Zeldovich and N. Semenov

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KINETICS OF CHEMICAL REACTIONS IN FLAMES¹

By Y. Zeldovich and N. Semenov

In part I of the paper the theory of flame propagation is developed along the lines followed by Frank-Kamenetsky and one of the writers. The development of chain processes in flames is considered. A basis is given for the application of the method of stationary concentrations to reactions in flames; reactions with branching chains are analyzed. The case of a diffusion coefficient different from the coefficient of temperature conductivity is considered.

INTRODUCTION

On investigating the process of the reaction of a given quantity of explosive mixture contained in a closed vessel a rapid increase is found in the velocity of the reaction as it proceeds, notwithstanding the decrease in the concentration of the reacting substances. Under certain conditions this increase in the reaction velocity, rate of heat liberation, and rate of increase of pressure leads to explosion accompanied by considerable thermal and mechanical disintegration.

Of great interest are the processes accompanied by the development of the reaction not only in time (as in the previous example) but also in space — that is, the phenomenon of the propagation of chemical reactions. In the present paper, the process of the quiet propagation of a flame will be considered, leaving detonation out of account. Propagation with supersonic velocity is essentially connected with the propagation of pressure waves. (See reference 1.) The transport phenomena responsible for the quiet propagation of

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flames have long since been pointed out. (See reference 2.) It is due mainly to the heat conductivity that the heated products of combustion ignite the fresh mixture. Considerably fewer references have been made to the part played by diffusion. Luther (reference 3) mentions the isothermal propagation of a chemical autocatalytic reaction in a water solution, a propagation connected with the diffusion of catalyzing products of the reaction, Lewis and Von Elbe (reference 4) emphasize in flame propagation, the role of diffusion of active centers, the consideration of which, however, does not enter in their involved and partially erroneous computations of the flame velocity in ozone.

In principle, all typical combustion phenomena might be described in terms of the simplest assumptions of an exothermal chemical reaction, the velocity of which (e.g., by the law of Arrhenius) increases with the temperature. Thus, without introducing any special assumptions as to the acceleration of a chemical reaction due to the accumulation of active centers, assumptions of a chain mechanism, and so forth, it was possible to develop the thermal theory of self-ignition (references 5, 15, and 18), the ignition of heated surfaces (reference 6), the theory of flame propagation (reference 7), the chemical kinetics of combustion in a jet and torch ignition of a gas (reference 8), and the propagation of detonation (reference 1). All these investigations merely constitute, however, the preliminary stage in the theory of combustion. Characteristic is the difficulty of finding real chemical reactions with a simple classical mechanism so that the acceleration of the reaction is connected only with the liberation of heat. It is necessary to choose such unusual substances as azomethane (reference 9), ozone (reference 4), or nitric oxide (reference 10).

Whatever the attitude taken by the authors of the schematic heat theories, the most important cases of the reactions of combustion, particularly combinations of fuels with oxygen of the air, are known to proceed by the chain mechanism. There arises the general problem of the introduction of rational empirical formulas to describe the dependence of the flame velocity on the various parameters in those cases where a detailed analysis of the reaction mechanism is impossible. These formulas should replace the entirely antiquated formulas that make use of the temperature of inflammation. (Le Chatelier) (reference 2), Nusselt (reference 11) or those based on apparently kinetic laws as the naive "law of mass action" of Stevens (reference 12), according to which the velocity of the flame in mixtures of hydrocarbons is

$$u \sim [\text{CO}]^2 [\text{O}_2]$$

Up to the present time the study of flame propagation, the measurement of the flame velocity, appears to be practically the only means for studying chemical reactions extending from 10^{-3} to 10^{-5} second at temperatures of 2000° to 3000° .

PROPAGATION OF THE REACTION IN SPACE

Dimensional Considerations

As has been pointed out in the introduction, a description of the propagation of the flame in space requires the introduction of the phenomena of transport.

The constants of the substance that characterize the transport are the coefficients of diffusion and heat conductivity. A dimensional analysis shows, however, that these magnitudes are not sufficient for constructing the velocity of the flame propagation. The dimensions of the diffusion coefficient are $D = \text{square centimeters per second}$.

From the thermal conductivity referred to the volumetric heat capacity of the medium is obtained the so-called temperature conductivity:

$$K = \frac{\lambda}{C_p \rho} = \frac{\text{cal/cm sec deg}}{\text{cal/g deg g/cm}^3} = \frac{\text{cm}^2}{\text{sec}}$$

In gases, as is known, K and D are very near each other in value. Were it not for the continuous liberation of new quantities of heat, the arising of new active centers, the propagation of a given quantity of heat or active centers would proceed with a gradually decreasing velocity.

In order to obtain the velocity of propagation of the flame it is necessary to introduce a certain characteristic of the medium for the chemical kinetics of the combustion reaction: namely, the reaction time, or the induction period. In this sense the "purely thermal theory" which uses only heat magnitudes is impossible. The formula of Mallard and Le Chatelier (reference 2) which does not contain the reaction time varying from one mixture to another, is simply erroneous.

If the time τ is introduced, the flame velocity is constructed in the following form with an accuracy up to a nondimensional factor

$$u \sim \sqrt{\frac{D}{\tau}} \sim \sqrt{\frac{K}{\tau}} \quad (1)$$

Transform this expression, making use of the relation:

$$K \sim D \sim ct; \quad \tau \sim \frac{vl}{c} \quad (2)$$

where

c is the velocity of motion of the molecules

l the length of free path

$v = 1/\omega$ the (average) number of collisions required for carrying on the chemical reaction

l/c the time for the free interval between two collisions

ω the probability of the reaction referred to a single collision

There is obtained approximately

$$u \sim \frac{c}{\sqrt{v}} \sim c \sqrt{\omega} \quad (3)$$

In agreement with the theory of the Brownian motion and diffusion of Smolukhovsky and Einstein this result is formulated as follows: The velocity of the flame is equal (in order of magnitude) to the mean velocity of the molecule over the portion of the path on which the molecule experiences v collisions.

The problem of the accurate formula for the flame velocity with all nondimensional factors, the problem of what conditions of the flame velocity the reaction time τ is to be referred to, the number of collisions v required for the reaction, and the probability ω of the reaction will next be considered.

SELF-IGNITION TEMPERATURE IN THE THEORY OF FLAME PROPAGATION

In the first papers on the theory of flame propagation, together with a correct conception of the part played by the heat conductivity, the concept of ignition temperature was widely used. (See references 2, 3, 13, and 14.) The simplifying theoretical assumption was made that the velocity of the chemical reaction is equal to zero below the ignition temperature; while at the ignition temperature the reaction velocity abruptly attains a high value.

Such a concept is unsuitable, primarily for the reason that, actually, from the point of view of the modern self-ignition theory, (references 5 and 15) the initial velocity of the chemical reaction does not undergo any abrupt change at the temperature of self-ignition. The essential difference in the behavior of the system above and below the self-ignition temperature appears only in the passage of a certain interval of time.

The self-ignition temperatures measured under the usual conditions correspond to periods of induction from several tenths of a second to several seconds. In a usual flame propagated with a velocity of about 1 meter per second for a width of zone of the order of 0.1 millimeter the entire temperature interval from the initial to the combustion temperature is traversed in about 10^{-3} second.

In the formula giving the results of computations with the ignition temperature (references 13 and 16)

$$u = \sqrt{\frac{K T_c - T_i}{\tau T_i - T_o}} \quad (4)$$

(where T_c is the temperature of combustion, T_i the temperature of ignition, T_o the initial temperature) is substituted the known theoretically and experimentally confirmed relation between the induction period or the reaction time τ and the ignition temperature:

$$\tau \sim e^{E/RT_i} \quad (5)$$

The flame velocity is obtained as a function of the ignition temperature which in this case is no longer considered constant, taking into account the fact that the ignition temperature according to (5) depends on the time associated with the system. In this case the maximum velocity of the flame is obtained for a choice

$$T_i = T_c - \frac{RT_c^2}{E} \quad (6)$$

that is, for T_i very nearly equal to T_c .

The experimental investigations of the dependence of the velocity on the initial temperature of the mixture all indicate that in the formula of type (4) T_i should be taken very high. The considerations show, within the frame of a theory that makes use of the concept of ignition temperature, the necessity for a large value of T_i approaching T_c . It may be seen that for the propagation of the flame the kinetics of the chemical reaction is essential, and at a temperature near that of the combustion.

DIFFUSION AND FIELD OF CONCENTRATIONS

Together with the heat conductivity it is necessary in every case to take account of the diffusion processes in the flame zone. In the flame the heating of the fresh mixture is accompanied by the occurrence in it of the products of combustion and a leaning of the fuel mixture.

Under the simplest assumptions, as regards the equality of the diffusion and temperature conductivity coefficients, the connection between the temperature and the composition of the mixture in the flame agrees with the relation between the temperature and the composition for adiabatic behavior of the chemical reaction at constant pressure. Finally, the same relation is obtained by the simple mixing (without loss of heat and without chemical reaction) of the fresh mixture taken at the initial temperature with the

products of complete combustion taken at the theoretical temperature of combustion.¹

The total enthalpy (heat content) of a unit mass (including the chemical energy) is the same at any point. It would, however, be entirely wrong to consider the result thus formulated as a special postulate or as a direct consequence of the law of conservation of energy, as is done by Lewis and Von Elbe (reference 4). Thus, in the case of hydrogen-containing mixtures in which the coefficient of diffusion of the hydrogen greatly exceeds the temperature conductivity of the mixture, the enthalpy is not at all conserved. Ahead of the flame front in the heating zone the supply of heat by the heat conduction is less than that conducted away by the chemical energy of diffusion of hydrogen in the zone of combustion. In the heating zone the enthalpy reaches a minimum, which, of course, in no way contradicts the first law of thermodynamics of the equality of the enthalpy before and after the passage of the flame. In mixtures with an insufficiency of hydrogen at a temperature near the combustion temperature the concentration of hydrogen is less than that computed by the postulate of the conservation of enthalpy in the ratio K/D (reference 16).

DETERMINATION OF THE FLAME VELOCITY FROM THE EQUATIONS

Having established a relation between the concentrations of the reacting substances, of the products of the reaction, and the temperature, consideration need be given only to a single differential equation for one of the above-mentioned magnitudes, for example, the temperature.

¹For the flame and for an adiabatic reaction (adiabatic explosion) the relation between the temperature and the concentration is the same, the substance passing through the same series of states. However, the kinetics, that is, the development of the processes in time are fundamentally different. Extremely slow at first (proportional to the velocity of the chemical reaction under the given conditions) the rise in temperature of the adiabatic explosion is replaced in the case of the flame by a much more rapid heating through the heat conductivity. On the other hand, the conduction away of heat by the fresh gas retards in the flame the last stage of attaining full combustion.

By passing from the consideration of two variables, the coordinates and the time (partial differential equation), to the coordinates of a system in which the flame is at rest, there is thus obtained an ordinary differential equation of the second order. In this equation the velocity of the flame propagation enters as a parameter.

$$-\frac{d}{dx} \lambda \frac{dT}{dx} + u C_p \frac{dT}{dx} = Q \quad (7)$$

where Q is the rate of heat liberation ($\text{cal}/\text{cm}^3\text{sec}$).

Two boundary conditions are imposed on the solution: for example,

$$T = T_0, \quad x = -\infty; \quad \frac{dT}{dx} = 0, \quad x = +\infty \quad (8)$$

The second condition may be transformed with the aid of equation (7) into the form

$$T = T_c, \quad x = +\infty \quad (9)$$

since combustion is considered without the giving off of heat to the outside.

The possibility of determining the parameter entering the equation, the flame velocity, is physically connected with homogeneous space. Formally this homogeneity appears in the circumstance that neither in the equation where x enters under the derivative sign nor in the boundary conditions, formulated for $x = \pm \infty$, does any finite value of x enter. As a result, in the general solution of the differential equation of the second order depending on the parameter u and two constants:

$$T = T(x, u, C_1, C_2) \quad (10)$$

one of the constants cannot be found. This becomes clear if (10) is written in the form

$$T = T(x + C_1, u, C_2) \quad (11)$$

From the two boundary conditions are found two magnitudes C_2 and u . Or else, the position of the flame might be fixed in space, giving the added condition for example,

$$T = \frac{T_c + T_o}{2}, \quad x = 0 \quad (12)$$

which together with the two boundary conditions (8) and (9) gives three equations for determining the three magnitudes; C_1 , C_2 , and u .

The relations are entirely analogous to the determination of the natural frequencies from the linear homogeneous differential equation of vibration with linear homogeneous boundary conditions. In this case the amplitude remains undefined and is determined by an additional normalizing condition.

On turning to a consideration of the flame, the part played by the homogeneity of the space will be described with the aid of an example (fig. 1).

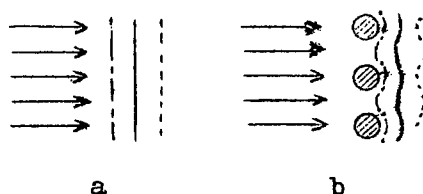


Figure 1

Consider a stationary flame in a gas flow, in one case in a homogeneous space (fig. 1, a), in the other in a space partitioned by a screen (fig. 1, b). In the first case, if the velocity of the flow is such that a perfectly stationary combustion is attained with a motionless flame front (heavy line) the flame front may either be more to the right or more to the left. It is this inconsequence which leads to the condition that for the smallest change in the flow velocity a slow motion of the flame arises from one position to the other, and so forth. A stationary state is possible only for a strictly determined "proper" value of the flow velocity. On the other hand, in the case of a flow partitioned by a

screen, the coordinates of the latter evidently enter the boundary conditions. The transformation of the solution into the form (11) will no longer be possible; to each value of the flow velocity corresponds a definite position of the flame front; a steady state is possible over a wide interval of flow velocities from the velocity at which there is a shift to the left to the velocity that gives rise to separation of the flame from the screen. A single condition of steady state does not lead to the determination of the proper value of the velocity of the flow. Taking into account the active centers or the heat liberation does not change the results as to the number of boundary conditions and number of arbitrary constants.

APPROXIMATE INTEGRATION OF THE EQUATION AND FINAL FORMULAS

The rapid increase in the velocity of the chemical reaction with the temperature leads to the result that in the flame where the entire temperature interval from T_0 to T_c exists the chemical reaction essentially proceeds at a temperature near that of the combustion temperature. (See sec. "Self-Ignition Temperature in the Theory of Flame Propagation".) This makes it possible to express the flame velocity by a comparatively uncomplicated formula (reference 7).

For an approximate integration of the equation it is noted that, if the temperature at which the chemical reaction proceeds is near the combustion temperature, the quantity of heat expended in raising the temperature of the reacting substance itself to the combustion temperature is not large. In the reaction zone the corresponding term in the equation is neglected. Practically the entire heat of the reaction is conducted by the heat conductivity to the as-yet nonreacting gas. The reader will find all details of the computation in the papers of Y. B. Zeldovich and D. A. Frank-Kamenetsky (reference 7) and N. N. Semenov (reference 5). Only the final formulas will be given here. The general formula is

$$u = \frac{1}{\rho_0 L} \sqrt{2 \lambda \int_{T_0}^{T_c} Q dT} \quad (13)$$

For a monomolecular reaction:

$$u = \frac{1}{\rho_o L} \sqrt{2\lambda g C_p \left(\frac{T_o}{T_c}\right) \left(\frac{n_o}{n_c}\right) \left(\frac{\lambda}{DC_p \rho}\right) \left(\frac{RT_c}{E}\right)^2 \exp\left(-\frac{E}{RT_c}\right)} \quad (14)$$

For a bimolecular reaction:

$$u = \frac{1}{\rho_o L} \sqrt{2\lambda g a_o \frac{C_p^2 \rho_o}{L} \left(\frac{T_o}{T_c}\right)^2 \left(\frac{n_o}{n_c}\right)^2 \left(\frac{\lambda}{DC_p \rho}\right)^2 \left(\frac{RT_c}{E}\right)^3 \exp\left(-\frac{E}{RT_c}\right)} \quad (15)$$

where

- u normal velocity of the flame (cm/sec)
- ρ_o the density of the initial mixture (g/cm³)
- L latent heat of the mixture (cal/g)
- λ heat conductivity of the reaction products at T_c (cal/cm sec deg)
- ρ density of the reaction products at T_c (g/cm³)
- Q rate of heat liberation (cal/cm³ sec)
- C_p heat capacity of the combustion products
- n_o/n_c ratio of number of molecules of initial mixture to number of molecules of reaction products by stoichiometric equation of reaction
- D coefficient of diffusion of reacting substance in reaction products at T_c (cm²/sec)
- E heat of activation of chemical reaction
- $k_c = g \exp(-E/RT_c)$ constant of chemical reaction velocity at T_c

CHAIN REACTION IN THE FLAME

In the majority of cases the chemical reaction in the flame proceeds by the chain mechanism, a fact which does not exclude the primary part played by the heat conductivity in the flame propagation since the probability and rate of branching of the chains, the number of active centers, the velocity of the chain reaction - all these parameters of the chain reaction greatly depend on the temperature.

Two fundamental types of chain reaction will be distinguished. In the first case, the instantaneous concentration of the active centers is determined by the equilibrium with the reacting substances, or in the more general case, by the method of stationary concentrations of Bodenstein, and is uniquely connected with the concentrations of the reacting substances. In this case, the velocity of the chain reaction is found to be expressible "classically" in terms of the macroscopically observed concentrations.

A necessary condition is the short lifetime of the active centers (in comparison with the duration of the reaction) a condition necessitating the rapid establishing of the stationary concentrations. From this it is seen that if the laws obtained in treating the reactions by the method of Bodenstein are satisfied with sufficient accuracy in tests in a closed vessel, uncomplicated by diffusion, then these same kinetic relations may be directly substituted in the equation for the flame propagation. Thus the velocity of propagation and the occurrence of gradients of the concentration are such that the characteristic diffusion time (over the width of the zone) is of the order of the time of the chemical reaction. This is seen from the fact that in the flame where the heat flow is of the order of all the liberated heat of reaction the diffusion flows also should be of the order of the quantity of substance burned in unit time. For an active product, however, the lifetime of which is much less than the reaction time, the former evidently will be much less than the characteristic diffusion time for a given steepness of the gradients, the diffusion will only slightly change the stationary concentration of the centers.

An example illustrating the foregoing considerations is the decomposition of ozone. According to Lewis and Von Elbe (reference 4), the reaction $O_3 \rightleftharpoons O_2 + O$ may be considered as very rapid so that the concentrations of O_3 and O are connecting by the law of mass action:

$$\frac{O}{O_3} \frac{O_2}{O_3} = f(T) \quad (16)$$

The velocity of the flame is determined by the progress of the slow reaction $O + O_3 = 2O_2$. In the expression for the velocity of the latter reaction are to be substituted the concentrations of O and O_3 connected by equation (16).

The second most important type of chain reaction differs (when conducted in a closed vessel) in the gradual autoacceleration of the reaction, increasing exponentially with the time. In the case where this autoacceleration is connected with the catalysis of the final stable products of the reaction, this is entirely understandable since in the zone of the flame where the reaction proceeds the concentration of the reaction products is known to be very large, differing little from the concentration of the products of the total combustion.

Thus, the reaction delay, the induction period associated with the accumulation of the reaction products observed on conducting the reaction in a closed vessel, is decreased in the flame as a result of diffusion. In a closed vessel, the induction period (logarithmic) depends on the initial concentration of active centers, and small additions of any active substances or the activation of the mixture by electric charges, and so forth, may considerably change the induction period. To change the flame velocity appreciably, however, is considerably more difficult. It is necessary to introduce a quantity of active centers of the order of the maximum quantity in the reaction zone. For the case where the active centers are the final products of the reaction, this maximum quantity is very large.

In the case where there is an accumulation of active unstable substances connected with the initial reacting substances not by stoichiometric but by kinetic equations the problem is more complicated, since it is necessary to take into account the subsequent nullification (recombination) of the active centers.

In order that it may be possible to speak of a well-defined second type of chain reaction, it is necessary that the recombination be small by comparison with the branching at the instant when the reaction has already passed through 70, 80, and 90 percent. Otherwise, the branching and recombination acting together determines a certain quasi-stationary concentration of active centers and brings about a return to the first type of chain reaction.

It maybe noted that the second type of chain reaction may give the phenomenon of an isothermal ("cold") flame, the propagation of the reaction by the diffusion of the active centers alone. The recombination of the latter narrows the limits of the propagation of the cold flame.

The recombination will be neglected far from the limits. In this case it may be said that the concentration of active centers will everywhere be proportional to the concentration of the final products. The factor of proportionality is no other than the probability of the branching referred to a unit link of the chain, that is, to a magnitude inverse to the length of the chain from one branching to the next.

For otherwise equal conditions, particularly for equal velocity of its occurrence in the reaction zone, the increase of the diffusion coefficient of an active center decreases its concentration in that zone. The afore-mentioned relation between the length of the chain and the concentration of final and active products requires a correction factor in the case where their diffusion coefficients are different.

Translation by S. Reiss,
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Authors (2)

Flame propagation

Flame propagation velocity - Measurement

Equations - Flame propagation